



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/GB98/03591 <b>(22) International Filing Date:</b> 2 December 1998 (02.12.98)  <b>(30) Priority Data:</b> 9725828.9                      6 December 1997 (06.12.97)                      GB  <b>(71) Applicant (for all designated States except US):</b> ALBRIGHT & WILSON UK LIMITED [GB/GB]; 210-222 Hagley Road West, Warley, West Midlands B68 0NN (GB).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> ZAKIKHANI, Mohsen [GB/GB]; 86 Croftdown Road, Harborne, Birmingham B17 8RD (GB).  <b>(74) Agent:</b> BARKER BRETTELL; 138 Hagley Road, Edgbaston, Birmingham B16 9PW (GB).		<b>(81) Designated States:</b> AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GD, GE, HR, HU, ID, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> FIBROUS SUBSTRATE TREATMENT  <b>(57) Abstract</b> <p>A method is provided of altering the chemical and/or physical functionality of a fibrous substrate (e.g. fibres, fabrics and fibre-resin composites) by the action of a polymeric composition containing at least one phosphono- or phosphino-component. The polymeric composition may include VPA, VDPA or hypophosphorous acid. The fibres may be cellulosic and/or non-cellulosic, or metal or ceramic. The method can be used, for example, to enhance the receptivity of a fibrous substrate to dyes.</p>		

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## FIBROUS SUBSTRATE TREATMENT

This invention relates to a method of treating a fibrous substrate so as to alter its chemical and/or physical functionality and to fibrous substrates  
5 treated by means of such a method.

The substrate may, for example, comprise fibres or a fabric.

The present invention further relates to the use of the method aforesaid to  
10 enhance the receptivity of a fibrous substrate to dyes.

The present invention yet further relates to the use of the aforesaid method to enhance the adhesion, to a fibrous substrate, of other substances.

15

Accordingly, the present invention provides, in a first aspect, a method of treating a substrate so as to alter its chemical and/or physical functionality, in which the substrate is reacted with an aqueous solution of a polymeric composition, said composition including at least one  
20 phosphono-component or at least one phosphino-component.

The substrate may comprise, for example, fibres or a fabric.

In accordance with the present invention, the phosphono-component or  
25 phosphino-component may consist essentially of vinylphosphonic acid (VPA), vinylidene-1, 1-diphosphonic acid (VDPA), a phosphono-substituted mono- or di-carboxylic acid, hypophosphorous acid or a salt, such as an alkali metal salt, of hypophosphorous acid.

For example, the phosphono-component may consist essentially of a homopolymer of VPA or of VDPA, or phospho-succinic acid.

5 The polymeric composition may further include one or more further (additional) components, such as unsaturated sulphonic acids, saturated or unsaturated carboxylic acids, unsaturated amides, primary or secondary amines, polyalkylene imines or amine-terminated polyalkylene glycols.

10 For example, the polymeric composition may consist essentially of a copolymer of vinylphosphonic acid (VPA) with vinylsulphonic acid (VSA), or with acrylic acid (AA), methacrylic acid (MAA) or acrylamide.

Alternatively, the polymeric composition may consist essentially of a copolymer of VDPA with VSA, or with AA, MAA or acrylamide.

15 As another example, the polymeric composition may consist essentially of a terpolymer of VDPA, VSA and either AA, MAA or acrylamide.

Again by way of example, the polymeric composition may consist  
20 essentially of the reaction product of VDPA and any one of the following:

- a) primary amines;
- b) secondary amines;
- c) polyethylene imines;
- 25 d) amine-terminated polyethylene or polypropylene glycols (Jeffamines);
- e) hypophosphorous acid or a salt thereof.

In a second aspect, the present invention provides a fibrous substrate treated by means of the method according to the first aspect of the present invention.

- 5 In a third aspect, the present invention provides the use of a method as hereinabove described to enhance the receptivity of a fibrous substrate to dyes.

Finally, the present invention provides the use of a method as hereinabove  
10 described to enhance the adhesion, to a fibrous substrate, of other materials.

Compositions according to the present invention may be applied to fibrous substrates which include cellulosic fibres. The cellulosic fibres are  
15 preferably natural cotton, but may be ramie, flax, linen, paper or cardboard or regenerated fibres (e.g. viscose or cuprammonium fibres) or partly etherified or esterified cellulose (e.g. cellulose acetate or propionate).

20 The substrate may contain both cellulosic and non cellulosic organic fibres, or consist entirely of non cellulosic organic fibres (e.g. 100% polyester fibres) or in some circumstances may consist entirely of cellulosic organic fibres (e.g. 100% cotton fibres).

25 The non cellulosic fibres are preferably polyester or polyamide, glass or carbon fibres, but may also be acrylic. The fibres may be metal or ceramic fibres. Other suitable non-cellulosic fibres include those of poly (p-phenylene benzo-bisthiazole) and poly (p-phenylene benzo-bisoxazole). The polyamide may be an aliphatic one, such as copolymers of a

polyamine (such as a diamine) preferably an alkylene diamine, e.g. of 4-12 carbon atoms and a polycarboxylic acid, e.g. a dicarboxylic acid, of 4-14 carbon atoms, such as an alkylene dicarboxylic acid (e.g. NYLON\* 66), or polylactams (such as NYLON\* 6). Alternatively, the polyamide may be  
5 an aromatic one, such as an aramid based on aromatic dicarboxylic acids and phenylene diamines. The substrate can contain at least 20% of cellulosic fibres and up to 80% of coblendable fibres e.g. 10-80% especially 25-80% of coblendable fibres (such as polyamides). However, the substrate preferably comprises cellulosic fibres and polyester fibres.  
10 The substrate usually contains up to 80% (e.g. up to 70%) polyester fibres and the remainder cellulosic fibres.

Substrates comprising at least 45% non cellulosic fibres such as polyester fibres, e.g. 45-100% polyester, are preferred, as are substrates  
15 comprising 30-78% cellulosic fibres and 22-70% polyester fibres, or 30-62% cellulosic fibres and 38-70% polyester fibres. The polyester is usually a condensation product containing structural units from an aliphatic alcohol, e.g. a dihydric alcohol, especially ethylene glycol or butane diol (or mixtures thereof) and an aromatic dicarboxylic acid, e.g.  
20 terephthalic acid, or a mixture thereof with other dicarboxylic acids, such as isophthalic acid, or sebacic acid.

The substrate fibres may be in the form of thread or non woven fabrics, but are preferably used in the form of woven fabrics. Mixtures of fibres  
25 (e.g. of cellulosic and other fibres) may be an intimate or non intimate mixture, but the fibres are preferably in the form of blends of cellulosic fibres and other fibres, (e.g. polyester fibres), as in cospun blends such as cotton/polyester or polyester/cotton staple fibre, but may be in the form of core spun yarn with a core of the other fibre, e.g. polyester-sheathed

cotton fibres. In a fabric, the warp and weft fibres are preferably the same, but may be different, e.g. one may be made from cotton fibres and the other from, say, polyester/cotton fibres or NOMEX\*/cotton. Thus in this specification the term "blend" also includes unions and union/blends as well as core/sheath fibres.

The method according to the present invention may be applied to the dyeing of fibres or fabrics.

10 The reactive dyeing of a fibre or fabric consisting essentially of cellulose (e.g. cotton, ramie, flax, linen, paper, cardboard) or of regenerated fibres (e.g. viscose or cuprammonium fibres) or of fibres and fabrics of cellulose acetate or cellulose propionate has hitherto required the addition of inorganic salts to the dye bath to enhance the receptivity of the fabric to the dye. Such salts require removal from the spent dye bath at the conclusion of the dyeing process.

The Applicants have found that the treatment of such fibres or fabrics with polymeric compositions according to the method of the present invention avoids the need to use inorganic salts, enhances the take-up of the dye by the fibre or fabric and enables the fibre or fabric to retain more of the dye after washing.

Non-cellulosic fibres or fabrics (e.g. polyester fibres or fabrics) have hitherto had to be dyed by means of disperse dyes. Disperse dyes do not react chemically with the fabric : they have to be physically "entrapped" in the fabric by the application of elevated temperature and pressure. Thus, a reactive dye would not be expected to "take" on a polyester fabric.

The Applicants have found that the use of a polymeric composition according to the method of the present invention to treat polyester fibres or fabrics results in the fibre or fabric becoming capable of being dyed by means of a reactive dye.

5

With regard to the dyeing of fabric blends (e.g. cotton/polyester blended fabrics), this has previously necessitated the use of two dyes : a reactive dye for the cotton and a disperse dye for the polyester.

10 The Applicants have found that the use of a polymeric composition according to the present invention to treat cotton/polyester blended fabrics results in the fabrics becoming capable of being dyed by means of a single reactive dye.

15 The use of the polymeric compositions of the present invention is equally applicable to fibres used in composites, wherein the adhesion at the interface between the fibres and the matrix is enhanced by the use of the polymeric compositions.

20 Such adhesion-enhancement has been evidenced by an increase in the force necessary to debond the fibres from the matrix and confirms interaction of the treated fibres, through the polymeric composition, with the matrix material (e.g. a resin). Suitable variation of the polymeric composition can be used to produce a "tight" or a "loose" composite,  
25 depending upon the desired properties of the composite.



The present invention will be illustrated by way of the following Examples.

### Example 1

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Polyester filament (about 18g) was made by melt-spinning polyester granules (available from Kodak Eastman as 0.78 IV) and placed in a dyeing bomb. 1 litre of a 75 g/l solution of the terpolymer of VPA/AA/VSA (5:4:1) was charged into this bomb. The temperature was raised to 130°C at a rate of 3 °C/min. The temperature of the bomb was maintained at 130°C for a further one hour. The bomb was then cooled to room temperature and the filament was removed and cured at 180°C for five minutes in an oven. The sample was then washed in water to remove any unbound polymer and dried.

15

The filament was then examined by scanning microscopy (SEM) and energy dispersive X-ray analysis (EDAX). The SEM images showed evidence for the presence of the terpolymer on the polyester, which was then confirmed by phosphorus dot maps of the images. These showed a significant increase in the number of dots (compared to the dot map for an untreated filament). The spectrum obtained by energy dispersive X-ray analysis also showed prominent phosphorus and sulphur peaks which were not present in the spectrum for an untreated filament. In addition, the level of absorbency of the treated filament was checked and showed that the filament had become hydrophilic.

25

## Examples 2 to 8

In the following Examples, fabric samples were treated with aqueous solutions of a vinylphosphonic acid-acrylic acid-sodium vinyl sulphonate  
5 terpolymer in which the mole ratio of the constituent monomers was 5:4:1 respectively.

### Example 2

- 10 A sample of plain-weave, undyed polyester fabric, 10cm by 5cm, was immersed in a solution containing 20% by weight of the VPA:AA:VSANa terpolymer and then hung up to dry. The sample was placed in a fan oven at 225°C for five minutes. After removal from the oven the sample was immersed in deionized water overnight and then stirred with three fresh  
15 aliquots of water to remove any unbound polymer. After this rinsing procedure the sample was dried in an oven at 95°C. Small pieces were cut from the centre of the fabric sample and examined by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX).
- 20 The SEM images (x500 magnification) showed evidence of a coating on the fibre surface and this was confirmed by phosphorus dot maps of the image. These showed a significant increase in the number of dots (compared to the dot map for an untreated fabric sample) such that the arrangement of the fibres was clearly reproduced. The spectrum obtained  
25 by energy dispersive X-ray analysis also showed prominent phosphorus and sulphur peaks (which were not present in the spectrum for an untreated fabric sample).

## Examples 3 to 5

Further samples of the polyester fabric of Example 2 were treated with terpolymer solutions of different concentrations as shown in TABLE I below. The sample treated with 5% terpolymer solution (Example 4) showed an enhanced dot map image and clear P and S peaks in the EDAX spectra. These elements were also detected in the sample treated with 2% terpolymer solution (Example 5).

TABLE I

10

Ex.	Terpolymer solution (%) w/w)	Cure conditions	Phosphorus dot maps of SEM image	EDAX spectrum
3	20	225°C/5 mins	Strong dot map image showing arrangement of fibres	Strong P and S peaks
4	5	225°C/5 mins	Increase in dots compared to untreated fabric - shows arrangement of fibres	P and S peaks
5	2	225°C/5 mins	No significant increase in dots compared to untreated fabric	Weak P and S peaks

**Examples 6 to 8**

Samples of NOMEX\* fabric were dipped in solutions of the VPA:AA:VSANa terpolymer and allowed to dry overnight. They were then put into a fan oven at 220°C for three minutes. After removal from the oven the samples were immersed in deionized water for an hour and then stirred with three fresh aliquots of water to remove any unbound polymer. After this rinsing procedure the samples were dried in an oven at 95°C. Small pieces were cut from the centre of the fabric samples and analysed as before.

EDAX spectra showed clear P and S peaks for all three samples, indicating that the terpolymer had become fixed to the fibres. A strong dot map image showing the arrangement of fibres was also obtained for the sample treated with 20% terpolymer solution (Example 7). The results are given in TABLE II:

**TABLE II**

Ex.	Terpolymer solution (%) w/w)	Cure conditions	Phosphorus dot maps of SEM image	EDAX spectrum
6	20	220°C/3 mins	Increase in dot compared to untreated fabric - shows arrangement of fibres	Strong P and S peaks
7	5	220°C/3 mins	No significant increase in dots compared to untreated fabric	P and S peaks
8	2	220°C/3 mins	No significant increase in dots compared to untreated fabric	Weak P and S peaks

**Examples 9 - 10**

More samples were prepared using the fabrics of Examples 3 and 6 respectively. These were then impregnated with a 50 g/l solution of aluminium hydroxide, dried and cured at 180°C for five minutes.

The EDAX spectra of the fabrics after treatment showed very strong peaks for aluminium, phosphorus and sulphur.

**10 Examples 11- 12**

More samples were prepared using the fabrics of Examples 3 and 6 respectively. These were then impregnated with a 1 M solution of potassium hydroxide, dried and cured at 180°C for five minutes.

15

The EDAX spectra of the fabrics after treatment showed very strong peaks for potassium, phosphorus and sulphur.

**Examples 13 - 14**

20

More samples were prepared using the fabrics of Examples 3 and 6 respectively. These were then impregnated with a 0.5 Molar solution of aluminium sulphate and dried and cured at 190°C for five minutes, rinsed thoroughly with water to remove any unbound material.

25

The EDAX spectra of the fabrics after treatment showed extremely strong peaks for aluminium phosphorus sulphur.

### Examples 15 - 16

More samples were prepared using the fabrics of Examples 3 and 6 respectively. These were then similarly impregnated with a 0.5 Molar solution of aluminium sulphate and dried without any subsequent curing at elevated temperature, rinsed thoroughly with water to remove any unbound material.

The EDAX spectra of the fabrics after treatment showed very strong peaks for aluminium, phosphorus, sulphur.

### Examples 17 to 18

The following Examples show the dyeing properties of a 100% polyester fabric modified with a polyethylene-imine phosphonate derivative. The derivative was applied to the fabric and the coloration of the resulting modified substrates with appropriate dyestuffs, together with the dyeing properties of a 100% cotton fabric treated with the polyethylene-imine phosphonate derivative, were investigated.

### Application of Phosphonate derivative

In the following Examples, "Polymer ITC973" denotes a polyethylene-imine phosphonate derivative of VDPA, available from Albright & Wilson UK Limited.

The polymer was supplied as a 20% w/w aqueous solution. The polymer was applied to a 100% polyester fabric by diluting to 10% w/w with distilled water and padding the resultant solution on to weighed samples of the fabric to a pick-up of about 80% (i.e. about 8% owf polymer was applied). The fabrics were then dried at 100 C for 5 minutes, then baked at 180 C for 5 minutes. The resultant fabrics were then washed thoroughly in hot, soapy water to remove unreacted polymer and allowed to dry.

In the case of the cotton fabric the application process was carried out as described hereinabove, except for the drying, which was carried out at room temperature overnight.

#### **Example 17**

##### **Reactive Dyeing of ITC973-Modified Polyester**

15

A series of reactive dyes utilising various different reactive chemistries was selected and applied to the modified polyester fabric using the following conditions:

20 2% owf dyestuff

1% Albegal B

Dye bath buffered to pH 5.5

Entered at 40°C, raised to 100°C and held for 60 minutes

25 The dyes selected were:

1. Remazol Brilliant Blue R (DyStar)- sulphatoethylsulphone

2. Lanazol Blue 3G (Ciba) - bromoacrylamido

3. Lanazol Red 2G (Ciba) - bromoacrylamido

4. Procion Red P-4BN (BASF)- monochlorotriazine

5.Procion Red H-E3B (BASF) - bis-monochlorotriazine

6.Sumifix Supra Brilliant Red BSF (Sumitomo) bifunctional (MCT/SES)

7.Sumifix Supra Brilliant Red GF (Sumitomo) - bifunctional (MCT/SES)

- 5 On completion of the dyeings, the fabrics were removed from the dye baths, rinsed under warm, running water and dried at room temperature. The exhaust dye baths were analysed using a uv/vis spectrophotometer and the exhaustion calculated as before.
- 10 In order to assess the level of fixation of the dyes to the substrate, samples of each dyeing were subjected to a C 06 wash fastness test:

5 g/l detergent

1 g/l sodium perborate

- 15 2 g/l sodium carbonate

50:1 liquor ratio

60 C for 30 minutes

- The colour strength (K/S) of each of the dyed samples, the washed  
20 samples and also of control fabrics (100% wool fabric dyed identically to the modified polyester) was measured using a DATACOLOR instrument.

### Example 18

#### Reactive Dyeing of ITC973-modified Cotton

25

Three reactive dyes utilising different reactive chemistries were selected and applied to the modified cotton fabric using the following conditions:

2% owf dyestuff



Dye bath buffered to pH 5.5

Entered at 40 C, raised to 100 C and held for 60 minutes

The dyes selected were:

5

1. Remazol Brilliant Blue R (DyStar) -sulphatoethylsulphone
2. Procion Red H-E3B (BASF) - bis-monochlorotriazine
3. Sumifix Supra Brilliant Red GF (Sumitomo) - bifunctional (MCT/SES)

10 On completion of the dyeings, the fabrics were removed from the dye baths, rinsed under warm, running water and dried at room temperature. The exhaust dye baths were analysed using a uv/vis spectrophotometer and the exhaustion calculated as before.

15 In order to assess the level of fixation of the dyes to the substrate, samples of each dyeing were soaped at the boil for 30 minutes.

The colour strength (K/S) of each of the dyed samples, the soaped samples and also of control fabrics (100% cotton fabric dyed identically to  
20 the modified cotton) was measured using a DATACOLOR instrument.

## Results

### Application of Phosphonate Derivatives

25

After final drying the fabric samples were weighed and the weight of each sample compared to that of the fabric before the application. Weight gains indicated that approximately 4% polymer had been fixed to the

fabric (i.e. about 50% of the applied polymer had reacted with and bonded to the polyester).

### Reactive Dyeing of ITC973-Modified Polyester (Example 17)

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The results of the dyeing experiments are given in the following TABLE:

COLOUR STRENGTH			
	Dye	973-Polyester	Washed 973-Polyester
10	1	40	32
	2	71	52
	3	91	76
	4	87	63
	5	59	31
15	6	66	33
	7	56	40

The results obtained from measuring the exhaust dye baths and comparing the colour strength of the washed polyester samples with the unwashed samples gives the following uptake figures:

20

	<u>DYE</u>	<u>% EXHAUSTION</u>	<u>% FIXATION</u>
25	1	82	80
	2	83	73
	3	99	83
	4	94	72
	5	99	52
	6	99	50
	7	98	71

### Reactive Dyeing Of ITC973-Modified Cotton (Example 18)

The results of the dyeing experiments on the ITC973-modified cotton are summarised in the following TABLE

5

#### COLOUR STRENGTH

	Dye	Untreated Cotton	973-Cotton	Soaped 973-Cotton
	1	13.7	128.5	98.7
	2	67.0	127.8	47.7
10	3	20.0	140.4	105.6

The results obtained from measuring the exhaust dye baths and comparing the colour strength of the soaped cotton samples with the unsoaped modified cotton samples gives the following uptake figures:

15

	<u>DYE</u>	<u>% EXHAUSTION</u>	<u>% FIXATION</u>
	1	92	77
	2	93	37
20	3	96	75

### Examples 19 to 21

The following examples relate to the effect of treatment, by means of  
 25 polymeric compositions according to the present invention, of aramid  
 fibres which are subsequently to be included in composites with matrices  
 such as epoxy-resins.

The fibres were treated with a copolymer of VPA and acrylic acid or with a terpolymer of VPA, AA and VSA and the forces required to debond the fibres from the resin matrix were measured

- 5 The fibres used were those available from Akzo Nobel under the name TWARON 1055 high-modulus fibres. (TWARON is a Registered Trade Mark).

10 The resin was a two-part, cold-curing epoxy resin comprising 100 parts by weight of LY5052 resin and 38 parts by weight of HY5052 hardener, both available from Ciba-Geigy. The resin contains a rigid novolak base and a low molecular weight reactive diluent, butane-1,4,diol diglycidyl ether. The hardener is a mixture of diamines, including isophorone diamine (35-45%) and 4,4-diamino-3,3'-dimethyl-dicyclohexyl methane  
15 (50-60%). The resin was cured at room temperature for 7 days and was found to have a Young's Modulus of about 3 Gpa and a shear yield stress of about 43 Mpa. The results of the "pull-out" tests are given in the TABLE below:

20	Example	Polymer used to treat fibre	COLD-CURE		HOT-CURE	
			Tf (c)	Tmax (d)	Tf	Tmax
25	19	None (control)	10 $\pm$ 3	35.7 $\pm$ 4.4	6.9 $\pm$ 2.7	39.7 $\pm$ 4.9
	20	Copolymer (a)	18	28 $\pm$ 3.4	14.7 $\pm$ 3.4	36.6 $\pm$ 4.2
30	21	Terpolymer (b)	11.8 $\pm$ 2.6	23.7 $\pm$ 6.2	13.3 $\pm$ 3.7	36.7 $\pm$ 5.8

**Notes:**

(a) A copolymer of VPA and AA

(b) A terpolymer of VPA, VSA and AA

5

(c)  $T_f$  = the frictional shear stress in the debonded region of the composite.

(d)  $T_{max}$  = the maximum shear stress (equivalent to the interfacial shear  
10 stress) of the composite.

## CLAIMS

1. A method of treating a fibrous substrate so as to alter its chemical and/or physical functionality, in which the substrate is treated with an aqueous solution of a polymeric composition, said composition including at least one phosphono-component or at least one phosphino-component.
2. A method according to Claim 1, in which the substrate comprises fibres or a fabric.
3. A method according to Claim 1 or 2, in which the phosphono-component consists essentially of vinylphosphonic acid (VPA).
4. A method according to Claim 1 or 2, in which the phosphono-component consists essentially of vinylidene-1, 1-diphosphonic acid (VDPA).
5. A method according to Claim 1 or 2, in which the phosphono-component consists essentially of a phosphono-substituted mono- or di-carboxylic acid.
6. A method according to Claim 3, in which the phosphono-component consists essentially of a homopolymer of VPA.
7. A method according to Claim 4, in which the phosphono-component consists essentially of a homopolymer of VDPA.
8. A method according to Claim 5, in which the phosphono-component consists essentially of phosphono-succinic acid.

9. A method according to Claim 1 or 2, in which the phosphino-component consists essentially of hypophosphorous acid or a salt of said acid.
- 5
10. A method according to any one of Claims 1 to 9 in which the polymeric composition further includes one or more components selected from the group consisting of unsaturated sulphonic acids, unsaturated carboxylic acids, unsaturated amides, primary amines, secondary amines, 10 polyalkylene imines and amine-terminated polyalkylene glycols.
11. A method according to Claim 10, in which the polymeric composition consists essentially of a copolymer of VPA and a compound selected from the group consisting of vinylsulphonic acid (VSA), acrylic 15 acid (AA), methacrylic acid (MAA) and acrylamide.
12. A method according to Claim 10, in which the polymeric composition consists essentially of a copolymer of VDPA and a compound selected from the group consisting of VSA, AA, MAA and acrylamide.
- 20
13. A method according to Claim 10, in which the polymeric composition consists essentially of a terpolymer of VDPA, VSA and a compound selected from the group consisting AA, MAA and acrylamide.
- 25
14. A method according to Claim 10, in which the polymeric composition consists essentially of the reaction product of VDPA and a compound selected from the group consisting of primary amines, secondary amines, polyethylene imines, amine-terminated polyethylene glycols and amine-terminated polypropylene glycols.

15. A method according to Claim 10, in which the polymeric composition consists essentially of the reaction product of VDPA and hypophosphorous acid or a salt of said acid.
- 5 16. A method of treating a fibrous substrate, substantially as hereinbefore described with reference to any one or more of the Examples.
- 10 17. A fibrous substrate treated by a method according to any one of the preceding claims.
18. A substrate according to Claim 17, which consists essentially of polyester fibres.
- 15 19. A substrate according to Claim 17, which consists essentially of fibres of glass, carbon, poly (p-phenylene benzo bisthiazole), poly (p-phenylene bisoxazole) or of acrylic fibres.
- 20 20. A substrate according to Claim 17, which consists essentially of aliphatic or aromatic polyamide fibres.
21. A substrate according to Claim 17, which consists essentially of metal or ceramic fibres.
- 25 22. A substrate according to Claim 17, which consists essentially of cellulosic fibres.
23. A substrate according to Claim 22, in which the fibres are cotton, wool, ramie, flax or linen.



24. A substrate according to Claim 17, which consists essentially of a fabric.
25. A substrate according to Claim 24, which consists essentially of a polyester fabric.
26. A substrate according to Claim 24, which consists essentially of a cellulosic fabric.
27. A substrate according to Claim 24, which consists essentially of a non-cellulosic fabric.
28. A substrate according to Claim 24, which consists essentially of a blend of cellulosic and non-cellulosic fabrics.
29. A substrate according to Claim 17, which consists essentially of a fibre/resin or fabric/resin composite.
30. A substrate according to Claim 29, which consists essentially of aramid fibres or aramid fabric in an epoxy-resin matrix.
31. The use of a method according to any one of Claims 1 to 16 to enhance the receptivity of a fibrous substrate to dyes.
32. The use of a method according to any one of Claims 1 to 16 to enhance the adhesion, to a fibrous substrate, of other materials.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/03591

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D06M15/356 D06P5/22 D06P1/52 C08J5/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D06M D06P C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 061 768 A (FARBWERKE HOECHST AKTIENGESSELLSCHAFT)  see page 3, line 68 - line 84; claims ---	1, 2, 17-20, 22-28, 31
X	DE 42 31 358 A (ROTTA GMBH) 24 March 1994  see page 4, line 67 - page 5, line 6 ---	1, 2, 17-20, 22-28
X	US 4 585 845 A (ENGELHARDT FRIEDRICH ET AL) 29 April 1986  see application example 2 ---	1-3, 17, 22-24, 26, 31
X	US 5 496 476 A (WILLIAMS JR WILLIAM A ET AL) 5 March 1996 see the whole document ---	1, 2, 17, 22-24, 26
-/-		

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

26 February 1999

Date of making of the international search report

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 94 01476 A (STOCKHAUSEN CHEM FAB GMBH ;KLIMMEK HELMUT (DE); KRAUSE FRANK (DE)) 20 January 1994</p> <p>see page 12, paragraph 2 - page 13, paragraph 2; claims; examples 22,28,29 ----</p>	<p>1-3,6, 10,11, 16-20, 22-28,31</p>
A	<p>EP 0 780 406 A (ALBRIGHT &amp; WILSON UK LTD) 25 June 1997</p> <p>see page 2, line 50 - line 57; claims -----</p>	<p>1-4,6,7, 10-14, 16-32</p>

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/03591

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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>D06M 15/356, D06P 5/22, 1/52, C08J 5/06</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/29957</b> <b>(43) International Publication Date:</b> 17 June 1999 (17.06.99)
<b>(21) International Application Number:</b> PCT/GB98/03591 <b>(22) International Filing Date:</b> 2 December 1998 (02.12.98) <b>(30) Priority Data:</b> 9725828.9                      6 December 1997 (06.12.97)                      GB <b>(71) Applicant (for all designated States except US):</b> ALBRIGHT & WILSON UK LIMITED [GB/GB]; 210-222 Hagley Road West, Warley, West Midlands B68 0NN (GB). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> ZAKIKHANI, Mohsen [GB/GB]; 86 Croftdown Road, Harborne, Birmingham B17 8RD (GB). <b>(74) Agent:</b> BARKER BRETTELL; 138 Hagley Road, Edgbaston, Birmingham B16 9PW (GB).		<b>(81) Designated States:</b> AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GD, GE, HR, HU, ID, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>With amended claims.</i>  <b>Date of publication of the amended claims:</b> 29 July 1999 (29.07.99)
<b>(54) Title:</b> FIBROUS SUBSTRATE TREATMENT  <b>(57) Abstract</b>  <p>A method is provided of altering the chemical and/or physical functionality of a fibrous substrate (e.g. fibres, fabrics and fibre-resin composites) by the action of a polymeric composition containing at least one phosphono- or phosphino-component. The polymeric composition may include VPA, VDPA or hypophosphorous acid. The fibres may be cellulosic and/or non-cellulosic, or metal or ceramic. The method can be used, for example, to enhance the receptivity of a fibrous substrate to dyes.</p>		

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## AMENDED CLAIMS

[received by the International Bureau on 12 March 1999 (12.03.99);  
original claims 10 and 14 amended; remaining claims unchanged (1 page)]

9. A method according to Claim 1 or 2, in which the phosphino-component consists essentially of hypophosphorous acid or a salt of said acid.
- 5 10. A method according to any one of Claims 1 to 9 in which the polymeric composition further includes one or more components selected from the group consisting of unsaturated sulphonic acids, unsaturated carboxylic acids, unsaturated amides, primary amines, secondary amines, and polyalkylene imines.
- 10 11. A method according to Claim 10, in which the polymeric composition consists essentially of a copolymer of VPA and a compound selected from the group consisting of vinylsulphonic acid (VSA), acrylic acid (AA), methacrylic acid (MAA) and acrylamide.
- 15 12. A method according to Claim 10, in which the polymeric composition consists essentially of a copolymer of VDPA and a compound selected from the group consisting of VSA, AA, MAA and acrylamide.
- 20 13. A method according to Claim 10, in which the polymeric composition consists essentially of a terpolymer of VDPA, VSA and a compound selected from the group consisting AA, MAA and acrylamide.
- 25 14. A method according to Claim 10, in which the polymeric composition consists essentially of the reaction product of VDPA and a compound selected from the group consisting of primary amines, secondary amines and polyethylene imines.